

Same-Sample Determination of Ultratrace Levels of Polybromodiphenylethers, Polybromodibenzo-*p*-dioxins/Furans, and Polychlorodibenzo-*p*-dioxins/Furans from Combustion Flue Gas

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The analytical method used for determination of polychlorinated dibenzo-*p*-dioxins and -furans (PCDDs/Fs) emissions from municipal waste combustors (MWCs) and other stationary sources was modified and validated to additionally allow for analysis of ultratrace levels of polybrominated diphenyl ethers (PBDEs) and polybrominated dibenzo-*p*-dioxins and -furans (PBDDs/Fs) from a common flue gas sample. Potential methodological problems related to physicochemical properties of brominated compounds, including UV- and temperature-induced debromination and degradation, were addressed. The selection of solvents, optimization of extraction time, and adaptation of the cleanup and fractionation steps increased mean recoveries of ¹³C₁₂-labeled PBDE and PBDD/F isotope dilution surrogates about 18% and 25%, respectively. The customary liquid chromatography isolation of PBDEs and PBDDs/Fs was replaced by optimization of high-resolution gas chromatography to separate target PBDFs (2,3,7,8-Br-substituted) from potentially interfering PBDEs before mass spectroscopic identification. The optimized method allowed quantitative determination of 56 mono- through decabromodiphenylether congeners, 15 congeners of 2,3,7- and 2,3,7,8-Br-substituted tri- to octabromodibenzo-*p*-dioxins and -furans, and all 210 polychlorinated dibenzo-*p*-dioxins and -furans present in the flue gas at levels of picogram to microgram per normalized cubic meter.

Polybrominated diphenyl ether (PBDE) is a common flame retardant that has been found in environmental matrixes worldwide.¹ The environmental levels of brominated diphenyl ether are of concern for the United States, where human breast milk and

blood levels of PBDEs are among the highest in the world.^{2,3} Interestingly, a new U.S. market basket survey measuring values of PBDEs in foods suggested that, contrary to polychlorinated dibenzodioxins/furans (PCDDs/Fs), food is not the major pathway of human exposure to PBDEs.⁴ Even though there has been significant research on brominated flame retardants, relatively little is known about their possible thermal breakdown products, polybrominated dibenzo-*p*-dioxins and -furans (PBDDs/Fs), which reportedly can exhibit toxicity and persistence similar to PCDDs/Fs and recently have been found in several environmental matrixes, including humans.^{5–9}

Combustion-related processes, including municipal solid waste incineration, are known to be a major source of atmospheric pollution with PCDD/F.¹⁰ The regulations concerning thresholds of PCDD/F emissions from stationary sources have triggered demand for development of analytical methods suitable for determination of trace levels of PCDD/F in flue gases and resulted in numerous standard methods worldwide (e.g., U.S. EPA Method 23 and European Standard EN 1948-1–3:2006).^{11–14} Widespread monitoring programs and effective implementation of environ-

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mental laws caused decreases in PCDD/F emissions from point sources in the industrialized nations over past 2 decades.^{10,15} For instance, the U.S. atmospheric emissions of PCDDs/Fs from municipal waste combustion have been reduced by approximately 99% between 1987 and 2000 (from 8905 g TEQ/year to 83.8 g TEQ/year, respectively).¹⁵ Therefore, extending analytical methods initially developed for PCDD/F determination to halogenated organics of growing environmental concern, e.g., bromodioxins/furans and their abundant precursors—PBDEs, is essential.

Highly sensitive, selective, and specific analytical methods are required for analysis of PBDD/Fs and PBDEs. It is because of the large number of congeners (209 and 210 possible PBDE and PBDD/F congeners, respectively), their low concentrations (PBDDs/Fs levels in the flue gases are usually very low, sometimes less than 0.1% of the level reported for PCDDs/Fs), and methodological problems related to thermal and photolytic degradation.^{16–25} Brominated compounds are in general more readily dehalogenated than chlorinated species, because of the smaller bond energy of C–Br (276 kJ/mol) than that of C–Cl (328 kJ/mol).²² Many experiments have shown reductive debromination to be a major photochemical decomposition pathway of brominated compounds, with the reaction rate depending on the bromine substitution pattern (higher brominated congeners and those with lateral bromines have reportedly shorter UV half-lives).^{23,24} Studies on decabromodiphenylether (DcBDE-209) degradation kinetics under natural sunlight resulted in estimation of half-lives as approximately 75 min (when DcBDE-209 was sorbed on kaolinite).²⁵ The half-lives of bromodioxins on soot or dust under direct sunlight exposure might be as low as several hours.⁹ Photodegradation of PBDEs and PBDDs/Fs have been also often demonstrated in various organic solutions.^{9,23–25} For instance, sunlight-induced half-lives for bromodioxins in organic solutions are reportedly as low as minutes (e.g., 0.8 min for 2,3,7,8-tetrabromodibenzo-*p*-dioxin (2,3,7,8-TeBDD)).⁹ The efficiency of UV-related debromination of bromodiphenylether in organic solvents reportedly depends on the number of bromine atoms, polarity of the solvent, and the presence of various surfaces (e.g., silica, gel, sand) in the solution.^{23,24} Photodegradation rates tend

to be higher for highly brominated compounds in less polar solvents and in the presence of a surface.^{23,24} DcBDE-209 is particularly sensitive to ultraviolet exposure in organic solvents; the UV degradation half-life of DcBDE-209 in a methanol/water solution was 30 min compared to 12 days for 2,2',4,4'-tetrabromodiphenylether (TeBDE-47).²⁴ The exposure of BDE organic solutions to UV light might not only cause debromination but also formation of PBDF.^{9,23} In experiments with UV and sunlight exposure of DecaBDE commercial formulation in hexane, a complex mixture of tri- to octabromodiphenylether (Tri- to OcBDE) congeners was detected as well as a large number of mono- to hexabrominated dibenzofuran (Mo- to Hx-BDF) congeners. After 16 h of the sunlight exposure the yield of the Mo- to Hx-BDFs formed was 10% of the total DecaBDE technical product.⁹ After 16 h UV exposure of toluene solution of DecaBDE technical product, yields of the 27 Mo- to Hx-BDFs formed were up to 1.2% of the initial amount of technical DecaBDE.²³ Thermodegradation issues are often associated with the residence time of highly brominated compounds' in the gas chromatographic (GC) systems, often with connection to injection port temperature.^{17,20,21}

Possible photodegradation and thermodegradation of PBDEs and PBDDs/Fs need to be taken into account while developing integrated analytical methods; however, overall extraction, cleanup, and fractionation methods for PBDDs/Fs and PBDEs analysis do not appear to be fundamentally different for those routinely used for PCDDs/Fs. The solvents recommended for removal of PBDEs and PBDD/Fs from environmental matrixes are usually toluene and methylene chloride, less often hexane and hexane/acetone mixtures.^{17,22,26} Nonpolar organic solvents (e.g., hexane) have high solubility for most bromoorganics but are not sufficient for extraction of matrixes rich in organic matter (containing many polar groups of amines, phenols, and carboxylic acids).¹⁷ The extraction methods (Soxhlet extraction, accelerated solvent extraction, pressurized liquid extraction, supercritical fluid extraction, microwave-assisted extraction) and times vary significantly among studies, i.e., from 6 to 24 h, depending on extraction procedure and sample volume.^{17,25,27} Conventional cleanup and fractionation techniques used for PCDDs/Fs (multilayer silica gel-, alumina-, activated carbon-column chromatography, Florisil cleanup, and gel permeation chromatography) reportedly work also for PBDEs and PBDDs/Fs.¹⁷ The main differences between procedures used for PBDEs and PBDDs/Fs versus those routinely employed for PCDDs/Fs are usually changes in composition/concentration of eluting organic solvents and modifications of the fractionation step (usually performed by means of liquid chromatography).^{17,27–33} For instrumental analysis of PBDEs and PBDD/Fs, both gas chromatography/mass spectrometry (GC/MS) and gas chromatography with electron capture detector (GC-ECD) are commonly

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used techniques (similar to PCDDs/Fs, high-resolution mass spectrometry, HRMS, is needed for analysis of PBDDs/Fs). Only recently have other techniques (gas chromatography two-dimensional mass spectrometry GC/MS/MS, gas chromatography time-of-flight mass spectrometry GC/TOFMS, two-dimensional gas chromatography time-of-flight mass spectrometry GC/GC/TOFMS, proton nuclear magnetic resonance ^1H NMR) been successfully applied to analysis of PBDEs in environmental matrixes and in technical bromodiphenylether mixtures.^{17,19,34,35}

The amount of published work on various analytical techniques for PBDE and PBDD/F analyses in environmental samples could suggest that methodology is well-established. However, the results of international calibration studies on brominated flame retardants (BFRs) and PBDDs/Fs confirmed that determination of certain bromoorganics is still an analytical challenge.^{20–22} Despite considerable improvement in performance of the analytical laboratories over the past few years, further development of extraction and cleanup procedures, and validation of instrumental methods analysis, are still needed.^{20–22}

The goal of this research was to validate an analytical method for analysis of trace levels of PCDDs/Fs and 2,3,7,8-substituted PBDDs/Fs, as well as PBDEs (including several “dioxin-like” congeners substituted in non-, mono-, and diortho positions), in combustion samples. Bromoorganics analysis required (1) comprehensive presampling, pre-extraction, and recovery spikes for the isotope dilution method, with internal standards covering the full degree of bromination of target PBDEs and PBDDs/Fs, (2) prevention of photo- and thermoinduced debromination by minimizing UV exposure, (3) selection of extraction solvents and optimization of sequential extraction time, (4) modification of elution solutions and steps for liquid chromatography-based cleanup, and (5) optimization of gas chromatographic system parameters (column length, temperature of injection port) for high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) analysis.

EXPERIMENTAL SECTION

Target Matrix and Sampling. Flue gas samples were collected in December 2006 from a U.S. municipal waste combustor (MWC). Sampling at postboiler (prior to the air pollution control system) and stack locations were performed. The flue gases were taken isokinetically using a modified version of U.S. EPA Method 23 (M-23) routinely used for sampling of PCDD/F from MWCs and other stationary sources.^{11,36} In this study, the M-23 sampling protocol was adapted for simultaneous sampling of PBDEs and PBDDs/Fs by addition of $^{13}\text{C}_{12}$ -labeled PBDE and PBDD/F presampling spikes and restrictive measures to avoid direct sunlight exposure (covering the sampling trains with aluminum foil during both sampling and transportation/handling). The

field blanks processed for sampling consisted of a sample cartridge containing XAD and filter that was spiked with the presampling spike solution, shipped to the field, installed on the sampler, and passively exposed at the sampling area (the sampler is not operated). Field blanks were sealed and returned to the laboratory for extraction, cleanup, and HRGC/HRMS analysis and were treated in exactly the same manner as a test sample.

Chemicals. The internal standard mixtures were prepared in-house from individual $^{13}\text{C}_{12}$ -labeled PBDEs and PBDDs/Fs solutions and commercially available custom-made $^{13}\text{C}_{12}$ -labeled PCDDs/Fs mixes. The composition of $^{13}\text{C}_{12}$ -labeled PBDEs and PBDDs/Fs spikes is given in the Supporting Information, Tables S-1 and S-2. The standard used for PBDEs identification and quantification was a mixture of brominated flame retardants (BFR-PAR; Wellington Laboratories, Canada), which consisted of mono- to decabrominated diphenyl ether congeners. The PBDD/F standard contained tetra- through octabromodioxins and/or furans congeners (EDF-5059, CIL Cambridge Isotope Laboratories Inc., U.S.A.). The standard used for chlorinated dioxin/furan identification and quantification was a mixture of standards containing mono- to octa-PCDD/F native and $^{13}\text{C}_{12}$ -labeled congeners designed for modified U.S. EPA Methods 0023a/8290 (ED-2521, EDF-4137A, EDF-4136A, EF-4134, ED-4135, CIL Cambridge Isotope Laboratories Inc., U.S.A.).²² All solvents were HPLC/GC/spectrophotometry grade ACS/HPLC certified (Burdick and Jackson, Honeywell, U.S.A.). Multilayer silica, carbon, and alumina columns were prepaced, disposable cartridges available from FMS Fluid Management Systems, Inc., U.S.A. The glass microfiber high-purity thimbles and filters were purchased from Whatman, U.S.A., and the XAD-2 resin was from Supelco, U.S.A.

Extraction. Extractions were initially performed according to procedures for PCDD/F removal from M-23 train samples by means of overnight Soxhlet extraction with toluene.¹¹ Toluene extraction has proven to be efficient for chlorodioxins analysis in similar matrixes, including the samples collected during a preceding sampling campaign at the same MWC.^{11,17,26,37} Nevertheless, we believe that toluene, because of its high boiling point, should not be used for extraction of potentially thermally labile brominated analytes, especially DcBDE-209. In addition possible photodegradation of PBDEs in toluene solutions or formation of PBDFs during overnight Soxhlet extractions was of concern, as long duration Soxhlet extractions at high temperature ($\sim 110^\circ\text{C}$, for 16 h) may promote copper-catalyzed dehalogenation and cyclization of PBDEs.²² Although copper was not added to the extract in the present study, the presence of copper or other transition metal catalysts in our study samples cannot be excluded. PBDE debromination/degradation and possible conversion of bromodiphenylethers to PBDFs in toluene could be sources of artifacts in this study. Therefore, the effect of adding a “soft” step, a short time extraction with a low boiling point solvent, was tested. Methylene chloride was selected as a solvent for the first step of the sequential procedure (similar to toluene, methylene chloride is a medium polar solvent, widely used for PBDDs/Fs and PBDEs extrac-

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tion; however, it has significantly lower boiling point than toluene: 39.5 °C vs 110.6 °C, respectively).^{17,19} Toluene remained the preferred solvent for the second step, as it is required for extraction of PCDDs/Fs from carbonaceous matrixes that contain soot particles.¹¹ The final method consisted of 3.5 h of methylene chloride extraction, followed by 16 h of extraction with toluene. The methylene chloride extract contained most of the brominated targets; for PBDEs, depending on the degree of bromination, the methylene chloride extracted an average of 99.7% of the total PBDEs, whereas the toluene extract contained 0.3% on average (1.64% maximum). Amounts of 94.1% and 8.9% of the total PBDDs/Fs extracted were found in the methylene chloride and toluene fractions, respectively. Fluorescent lights in the laboratory were shielded with ultraviolet-absorbing filters, and incandescent lighting was used. The extraction process itself was performed in complete darkness, where the sash of the fume hood was covered with aluminum foil. All raw extracts were concentrated using three-ball Snyder columns, filtered, and concentrated further in nitrogen to 1 mL using the automated evaporation TurboVap workstation.

Cleanup and Fractionation. For determination of PCDDs/PCDFs and PBDDs/PBDFs/PBDEs, one-half and one-quarter of the extract was cleaned and fractionated using an automated liquid chromatography multicolumn Power Prep/Dioxin System (FMS Fluid Management Systems, Inc., U.S.A.). The remaining one-quarter of the extract was archived. Prior to the automated cleanup process, extracts were concentrated and diluted in *n*-hexane, then loaded and pumped sequentially through individual sets of FMS proprietary columns: multilayer silica (4 g acid, 2 g base, and 1.5 g neutral), followed by a basic alumina (11 g) column and, in the case of PCDDs/Fs, also a carbon column (0.34 g). The cleanup of PBDDs/Fs and PBDEs required use of 100 mL of 100% methylene chloride to elute those compounds from the alumina column, instead of 120 mL of 50% methylene chloride in hexane used for elution of PCDDs/Fs. The carbon column was problematic for the cleanup of highly brominated PBDEs and PBDD/Fs, notably affecting their recoveries (probably resulting from the steric hindrance effect, which theoretically should increase in the order F < Cl < Br < I and depends on the bulk of the substituent halogens); hence, the use of the carbon column for the bromoorganics was suspended. Recoveries for cleanup of mixture of PBDEs/PBDDs/PBDFs standards employing a carbon column are given in Figure S-2 of the Supporting Information. Even though the matrix effect was not tested in those experiments, recoveries obtained are in the range of 0.30–53.1% for PBDEs and 10.4–35.4% for PBDDs/Fs, therefore much lower than that obtained for cleanup with the suspended carbon column step used for samples of flue gas analyzed in this study, depending on bromination degree: 10.1–87.9% for PBDEs and 53.9–108.9% for PBDDs/Fs, respectively. The details on PCDDs/Fs and PBDDs/PBDFs/PBDEs cleanup and fractionation method are given in the Supporting Information, Figure S-1. The aliquots of the PCDDs/Fs and PBDDs/PBDFs/PBDEs fractions were concentrated to a final volume of 100 μ L using the automated TurboVap concentration workstation (Caliper Life Sciences, Inc., U.S.A.)

and N-Evap nitrogen blow-down evaporator (Organomation Associates, Inc., U.S.A.). Final extracts were transferred to amber glass vials and refrigerated until analysis.

HRGC/HRMS Analysis. Concentrations of all target analytes were determined by means of HRGC/HRMS using a Hewlett-Packard gas chromatograph 6890 series equipped with a CTC ANALYTICS Combi PAL autosampler (CTC Analytics, Switzerland purchased from LEAP Technologies, U.S.A.) coupled to an Autospec Micromass Premier (Waters Inc., U.K.) double-focusing high-resolution mass spectrometer.

HRGC System. For analysis of mono- through octa-BDEs and tri- through hexa-BDD/Fs, the GC was equipped with long (60 m) capillary columns: HP-5 (SGE Analytical Science Pty. Ltd., Australia) or DB-5 (J&W Scientific, U.S.A.). For nona-through deca-BDEs and hepta- through octa-BDD/Fs analysis a short (15 m) HP-5 column was used. Both short and long columns were of 0.25 μ m film thickness \times 0.25 mm i.d. For analysis of mono- through octa-CDDs/Fs, a 60 m DB-Dioxin (J&W Scientific, U.S.A.) column was used (0.15 μ m film thickness \times 0.25 mm i.d.).

The GC oven temperature for PBDE and PBDD/F analysis was programmed from 130 to 230 °C at 15 °C min⁻¹ (5 min hold), then to 280 °C at 10 °C min⁻¹ (60 min hold), and then to 320 at 15 °C min⁻¹ with a final hold time of 35 min on the 60 m column and from 130 to 320 °C at 10 °C min⁻¹ (15 min hold) for the 15 m column. The temperature program for PCDD/F was from an initial temperature of 130 to 260 °C at 6 °C min⁻¹ with a final hold time of 50 min. The carrier gas (helium) flow rate was 1 and 1.5 mL min⁻¹ for brominated compounds analysis (short and long column, respectively) and 0.9 mL min⁻¹ for chlorinated compounds. Two microliters (2 μ L) of the extract was injected under splitless mode (injection port temperature set as 270 and 300 °C for chlorinated and brominated target analysis, respectively).

HRMS System. The HRMS was operated in an electron impact (35 eV and 650 μ A current) selective ion recording (SIR) mode at resolution $R > 10\,000$ (5% valley). The temperature of the ion source was 280 °C for the PBDE and PBDD/F analyses, whereas for PCDD/F, the ion source was kept at 250 °C. The two strongest ions in the molecular cluster were monitored in every retention time window for each native and labeled PBDD/F, PCDD/F, and PBDE based on mass spectroscopy libraries and literature data, unless interferences were present. In the case of the nona- and decabrominated diphenyl ether congeners, the BDE – 2Br fragment ion was monitored (ions selected for HRMS SIR of PBDEs and PBDDs/Fs are given in the Supporting Information, Table S-2). For the PBDFs fragment ion, –COBr was used to confirm the assignment of several bromodibenzofuran congeners which were not present in the calibration standards. For the data collection, Mass Lynx software version 4.1 was used (including Target Lynx 4.1. for processing and quantitation).

Quality Control/Quality Assurance. Sorbent (XAD-2) cartridges were prespiked with a mixture containing ¹³C₁₂-labeled analogues of selected chlorinated and brominated target compounds before sampling. All samples, including blanks, were spiked with internal standards before extraction and again before analysis (isotope dilution). Laboratory method blanks representing the background contributions from glassware,

extraction, and cleanup were analyzed by HRGC/HRMS in exactly the same manner as the test samples.

The HRMS was tuned daily or prior to each sample acquisition. Static resolving power checks were performed daily with a perfluorokerosene (PFK) calibration standard to achieve required resolution of 10 000 (5% valley). Peak responses for each of the two selected molecular cluster ions were at least 3 times the noise level ($S/N > 3$), and the bromine/chlorine isotope ratio for the two molecular cluster ions was within $\pm 20\%$ of the correct isotope ratio; otherwise they were considered below the limit of detection. To produce the calibration curves sets, five calibration solutions were prepared for PCDD/Fs, PBDDs/Fs, and PBDEs (CS-1 to CS-5). The medium concentration (CS-3) standard was used for calibration verification according to requirements of EPA Method 8290 and EPA Method 1614.^{38,39} The PBDE calibration standard contained 41 mono- through deca-BDE native congeners, as well as all congeners present in $^{13}\text{C}_{12}$ -labeled solutions—the surrogate standard, cleanup standard, and injection internal standard. The calibration solution of PBDD/F contained 11 native 2,3,7,8-substituted analogues of polybrominated dibenzo-*p*-dioxin and dibenzofuran and appropriate $^{13}\text{C}_{12}$ -labeled compounds. The calibration solution of PCDD/F contained native mono- through octachlorinated 2,3,7,8-Cl-substituted dibenzo-*p*-dioxin and furan and suitable $^{13}\text{C}_{12}$ -labeled analogues, according to modified U.S. EPA Methods 0023A/8290.^{11,36,38} The list of all native PBDE and PBDD/F analytes is given in Tables S-3 and S-4 of the Supporting Information. The quality assurance/quality control (QA/QC) measures in sampling, analysis, and evaluation of data incorporate system and laboratory performance requirements of the U.S. EPA Method 1614 for PBDEs and the U.S. EPA Method 23 and 8290 for PCDDs/Fs and PBDDs/Fs.^{11,38,39}

RESULTS AND DISCUSSION

Simultaneous Sampling of Bromoorganics and Chloroorganics. All the requirements of the M-23 protocol are assumed to be critical for collection of representative gas samples for bromoorganics in this study. In addition, measures to avoid direct/indirect sunlight exposure of the sample (not required for PCDDs/Fs sampling) are considered to be critical for obtaining satisfactory recoveries of the brominated analytes in this study. A good indication of sampling efficiency is surrogate recovery, measured relative to the internal standards. The presampling surrogate recoveries in this study, 102% ($\pm 6.6\%$ SD) for PCDDs/Fs, 105.4% ($\pm 10.8\%$ SD) for PBDDs/Fs, and 94.9% ($\pm 9.4\%$ SD) for PBDEs, respectively, are well within the range of 70–130% recommended by U.S. EPA Method 23 for chlorinated dioxins.¹¹

Optimization of Extraction. The sequential Soxhlet method used in this study with methylene chloride (3.5 h) and toluene (16 h; “overnight”) enabled effective removal of trace amounts of chlorinated and brominated targets from the carbonaceous matrix core of sampled material. However, filters in this study had

relatively light carbon loads compared to samples previously collected from this MWC source. Therefore, applicability of our method to carbon-rich matrixes from other combustion sources should be tested. Because M-23 requires toluene use for PCDD/F removal,¹¹ methylene chloride and toluene extracts were combined before further steps of PCDD/F analysis.

Selection of both the extraction medium (solvent) and time of extraction had a significant impact on the recoveries of brominated target compounds. As demonstrated in Figure 1, introduction of the short (“soft”) methylene chloride step to the Soxhlet extraction enhanced the recoveries of brominated analytes by approximately 20% (25% on average for PBDEs and 18% for PBDDs/Fs, respectively) when compared to extraction with toluene only (both extractions were performed with restricted exposure to UV light). Obviously, these methodological adaptations of extraction aided avoiding thermo- and photodegradation-related losses of brominated analytes in the present study.

The effect of the extraction solvent on recoveries of PCDDs/Fs was certainly less prominent than in the case of brominated analytes. The recoveries of PCDD/F $^{13}\text{C}_{12}$ -labeled internal standards were similar for samples extracted with methylene chloride and toluene, compared to those treated with toluene only. Interestingly, higher chlorinated congeners exhibited better average recoveries in samples extracted by sequential procedure (Figure 1b). This may be due to the slower photolytic degradation rate of lower chlorinated dioxins and furans which tend to be more stable in organic solvents than their brominated analogues; the photolytic reaction of 1,2,3,4-TeBDD in 2,2,4-trimethylpentane (iso-octane) is very rapid, with a half-life of 3 min, compared to 380 min for 1,2,3,4-TeCDD.⁹

Optimization of Cleanup and Fractionation. The multistep cleanup and fractionation of the FMS Power-Prep system has been extensively used for PCDD/F purification from numerous environmental matrixes. However, the applications of Power-Prep for purification of brominated compounds are relatively less studied.⁴⁰ In this study, the method used for chlorinated dioxins/furans was not only modified with regard to solvent concentration and volumes but also modified by eliminating the last fractionation step (carbon column) for bromoorganics (Figure S-1 of the Supporting Information illustrates differences of the cleanup and fractionation scheme used for chlorinated and brominated analogues in this study). Importantly, the use of preppacked columns minimizes the contact of the column bed with laboratory air particles, which might contain flame retardants in high concentrations (BDE-47, -99, -209 in indoor household dust were reported at average concentrations of 51, 79, 470 ng g⁻¹, respectively).⁴¹ Both the minimized exposure of the sample to dust and the use of relatively small volumes of solvents in the automated fractionation process should be considered as particularly valuable in the decabromodiphenyl analysis context where, reportedly, high procedural blanks are often a problem.^{20,21} Only seven PBDE congeners were detected in some of the procedural and field blanks in this study (TeBDE-47, PeBDE-99, PeBDE-100, NoBDE-206, NoBDE-207, NoBDE-208, and DcBDE-209); however, their concentration never exceeded their concen-

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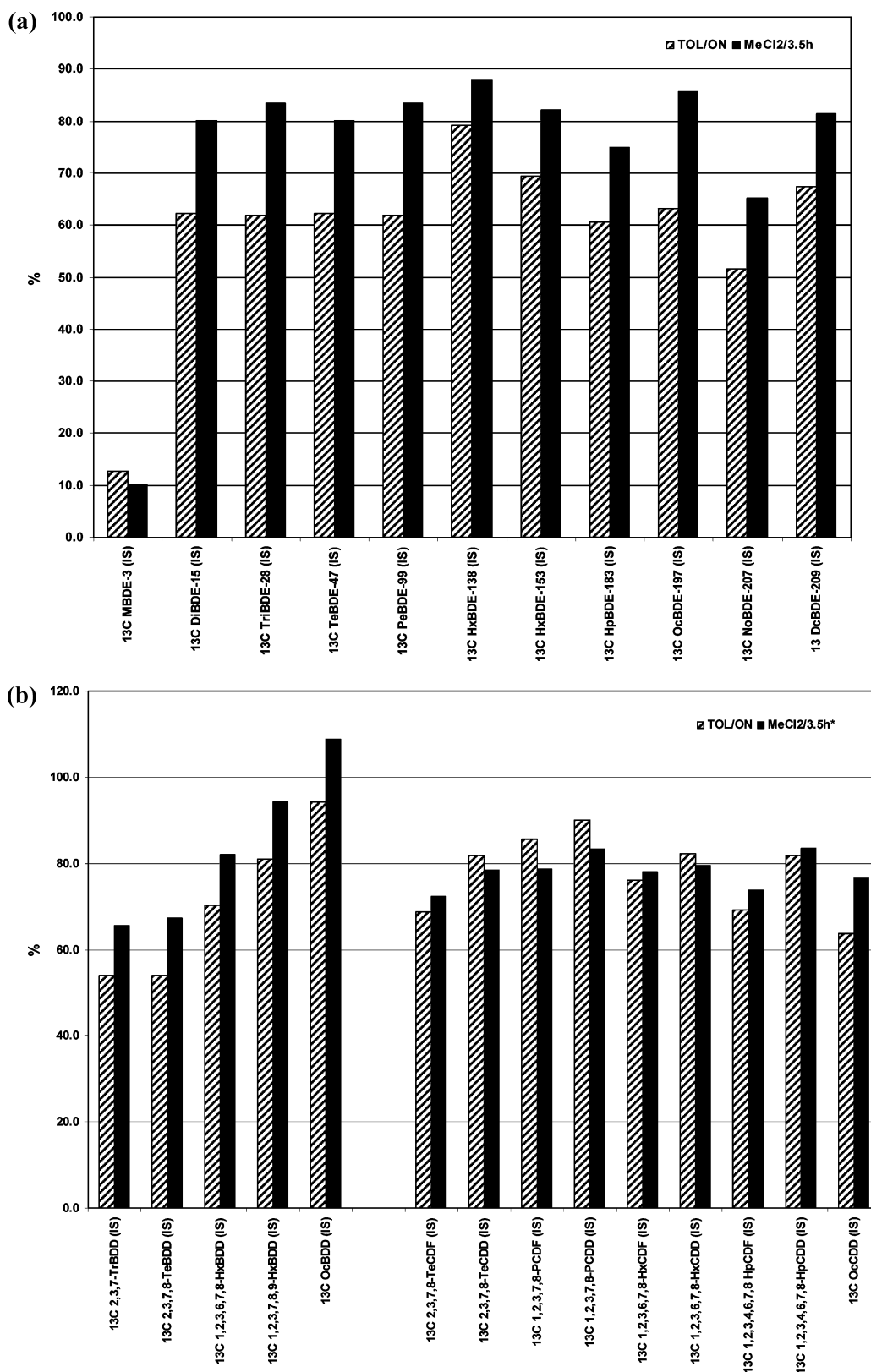


Figure 1. Comparison of the extraction solvent effect on recoveries of (a) bromodiphenylethers, extracted overnight in toluene only (TOL/ON) vs extracted in methylene chloride only for 3.5 h (MeCl₂/3.5 h), and (b) brominated dioxins/furans, extracted with toluene overnight only (TOL/ON) vs extracted with methylene chloride only for 3.5 h (MeCl₂/3.5 h), compared to recoveries of chlorinated dioxins/furans extracted with toluene only (TOL/ON) vs methylene chloride followed by toluene overnight (MeCl₂/3.5 h*), respectively. Given recoveries are calculated for the complete analytical procedure, i.e., after cleanup and fractionation; IS = internal standard; PBDE no. *n* = PBDE IUPAC number. *: PBDD/F = 3.5 h methylene chloride vs toluene only, PCDD/F = 3.5 h methylene chloride + toluene overnight vs toluene only.

trations in the flue gas (total concentration of PBDEs detected in blanks was on average 2.8% of average total PBDEs detected).

PBDDs/Fs were not detected (<LOD) in the procedural and field blanks in this study.

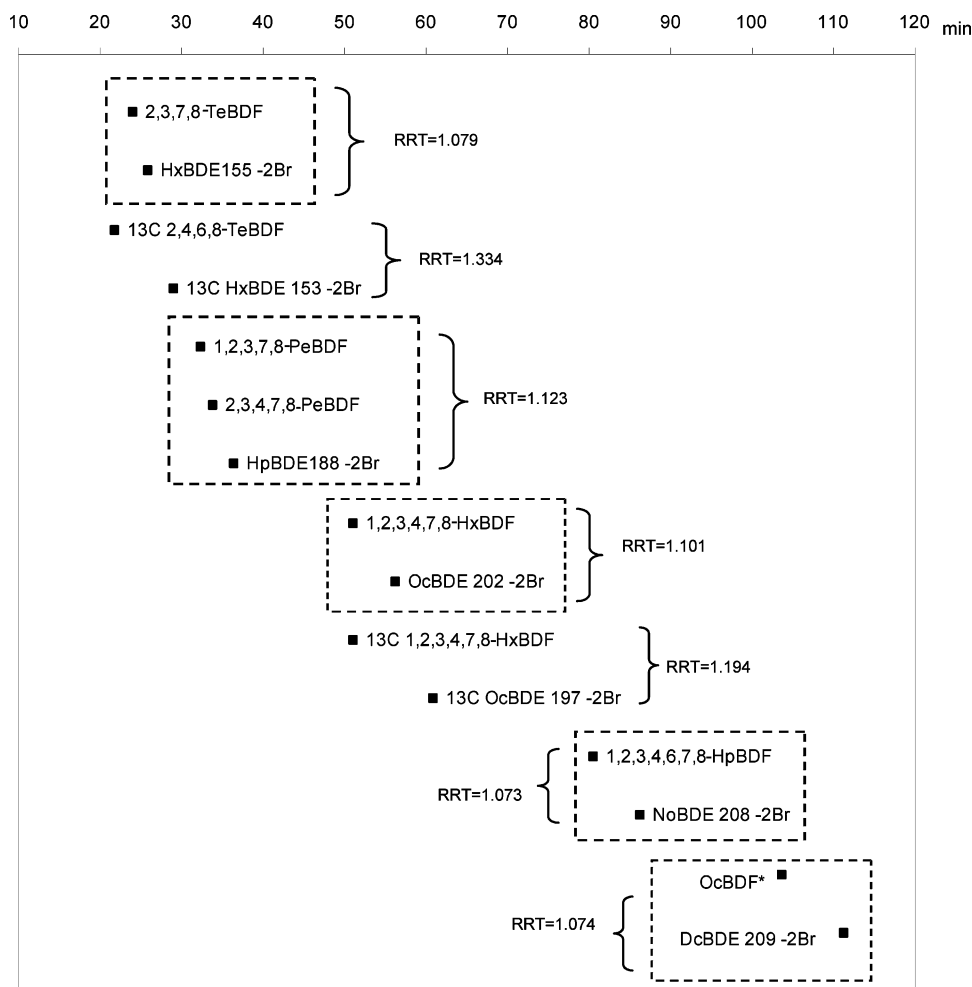


Figure 2. HRGC separation of target native PB_nDF / $^{13}C_{12}$ -labeled PB_nDF congeners and potentially interfering $PB_{n+2}DE - 2Br$ congeners on the 60 m DB-5 capillary column; relative retention times (RRTs) are calculated for the first eluting PBDE congener in the group as assigned based on the PBDE window mix solution (BDE-WD; Wellington Laboratories, Canada) compared to the retention times of all target PBDFs quantified. *: not present in the calibration standard; assignment based on isotope theoretical ratios and retention times of OBDD.

Optimization of the HRGC/HRMS System. The selection of a capillary column for a chromatographic separation of PBDEs and PBDDs/Fs was aided by several published retention time (RT) databases and the recent intercalibration studies results.^{22,42–44} The narrow (0.25 mm) and very long (60 m) 5% phenyl-dimethyl polysiloxane type columns (DB-5, HP-5) used in present study served extremely well for separation of mono- through decabrominated diphenyl ethers (Figure S-3 of the Supporting Information). The use of a 60 m column allowed separation of PBDE congeners that coelute on shorter columns (e.g., normally co-eluting HxBDE-156 and -169 were separated on the 60 m DB-5, as demonstrated on Figure S-3b of the Supporting Information). More importantly, the use of a 60 m column enabled HRGC separation of all 2,3,7,8-substituted target PBDFs from their potentially interfering PBDEs (PB_nDF s and $PB_{n+2}DE$ after loss of 2Br). HRGC separation of target native 2,3,7,8-PBDFs, as well as $^{13}C_{12}$ -labeled 2,3,7,8-PBDFs, from their potentially interfering PBDE congeners on the 60 m DB-5 capillary column

is shown in Figure 2 (optimum settings for correct retention time windows were verified experimentally by analyzing window-defining mixture of mono- through deca-BDE parallel to PBDD/F standards; chromatograms are available in the Supporting Information, Figure S-4).

Because we experienced sensitivity problems in the determination of DcBDE-209 and octabromodibenzo-*p*-dioxin/furan (OcBDD/F) on the 60 m 5% phenyl/95% dimethyl polysiloxane type (both HP-5 and DB-5) columns, we decided to use a multicolumn technique, with a second, shorter, 15 m capillary column. The use of a shorter column, to reduce PBDEs and PBDDs/Fs residence time in the GC system, likely minimized thermal degradation of the highly brominated targets and, together with optimization of the injection port temperature, has improved sensitivity for problematic compounds. Retention time windows of nona- to deca-BDEs against hepta- and octa-BDD/F are available in the Supporting Information, Figure S-5. Numerous injection techniques (on-column, PTV, splitless) were successfully used for bromoorganics analysis.^{17,19,22} However, due to widespread accessibility in analytical laboratories, splitless injections with an autosampler are most often used for analysis of PBDEs and PBDDs/Fs.^{17,19,22} The temperature of the injector for splitless injections is normally between 250 and 300 °C.^{17,19,22} In this study,

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Table 1. Summary of the PBDE and PBDD/F Isotope Dilution Analysis, Concentration Range Where Linearity Was Tested (Five-Point Calibration Curve, CS-1–CS-5), R^2 (Correlation Coefficient), RRFi, (Relative Response Factor of Analyte i), and Repeatability (Short-Term Relative Standard Deviation Estimated Based on 10-Times Analysis of Middle Concentration [CS-3] PBDE and PBDD/F Calibration Standard)^a

congener	IUPAC no.	CS-1–CS-5 dynamic range (ng·mL ⁻¹)	R^2	RRFi (mean)	repeatability (RSD %)
4-MoBDE	3	10–100	0.998	0.865	1.6
4,4'-DiBDE	15	10–100	0.998	0.603	0.91
2,4,4'-TriBDE	28	10–100	0.998	0.931	0.80
2,2',4,4'-TeBDE	47	20–200	0.998	0.891	1.0
2,2',4,4',5-PeBDE	99	20–200	0.998	0.919	0.83
2,2',3,4,4',5'-HxBDE	138	20–200	0.997	0.974	4.3
2,2',4,4',5,5'-HxBDE	153	20–200	0.997	0.811	2.1
2,2',3,4,4',5',6-HpBDE	183	40–400	0.998	0.857	2.4
2,2',3,3',4,4',6,6'-OcBDE	197	40–400	0.999	0.827	2.8
2,2',3,3',4,4',5,6,6'-NoBDE	207	100–1000	0.998	0.902	2.3
DcBDE ^b	209	100–1000	0.983	0.282	5.5
2,3,7,8-TeBDD		50–500	0.998	0.808	3.1
2,3,7,8-TeBDF		50–500	0.993	1.012	3.2
1,2,3,7,8,9-HxBDD ^c		50–500	0.994	1.599	6.0
OcBDD		50–500	0.976	0.864	9.2

^a Relative response factor (RRFi) of the native PCDDs/Fs, PBDDs/Fs, and PBDEs (As) in the calibration standard was relative to its labeled internal standard (Ais) and was determined using the area responses of both the primary and secondary exact m/z 's of compound specified in Supporting Information Table S-2 for each calibration standard, as follows: $RRFi = (A1s + A2s)Cis / (A1is + A2is)Cs$, where A1s and A2s = the measured areas at the primary and secondary m/z for the target, A1is and A2is = the measured areas at the primary and secondary m/z for the internal standard, Cis = the concentration of the internal standard, and Cs = the concentration of the compound in the calibration standard. ^b RRF against ¹³C₁₂-labeled NoBDE which was used for quantification of DcBDE (due to observed variability between different lots of ¹³C₁₂-labeled DecaBDE standard). ^c RRF against ¹³C₁₂-labeled 1,2,3,7,8,9-HxBDD from ¹³C₁₂-labeled 1,2,3,6,7,8/1,2,3,7,8,9-HxBDD solution.

optimal sensitivity for lower and higher brominated compounds was achieved when the temperature of the injection port was set at 300 °C for 2 μ L splitless injection. Higher (320 °C) and lower (270 °C) injection port temperatures tested in this study resulted in poorer sensitivity. The high temperature (>320 °C) is often reported to promote degradation of highly brominated compounds, especially DcBDE, whereas lower temperature of the injection port might have had a negative effect on volatilization efficiency of compounds with high molecular mass.^{19,21,22,25} The temperature of the ion source has not been optimized in our study; it has been set at 280 °C based on literature data.¹⁷ After the adaptation of the HRGC system, the electron impact (EI)-HRMS detection method used in this project has resulted both in good sensitivity (femto- to picogram per microliter instrumental detection limits) and selectivity (Supporting Information, Figures S-6–S-8).

Validation of the Method. The optimized method allowed quantitative determination of 56 mono- through decabromodiphenylether congeners, 17 congeners of tri- to octabromodibenzo-*p*-dioxin and furan (13 congeners substituted in 2,3,7,8-positions), and all 210 polychlorinated dibenzo-*p*-dioxins and furans at levels of picogram to microgram per normalized cubic meter of flue gas (average total concentrations of all target compounds in the flue gas are given at Figure S-9 of the Supporting Information; concentrations of analytes in the flue gas varied significantly during steady state and transients operating condition of the MWC boiler tested).^{45,46} The recovery rates were 77.7% ($\pm 11.7\%$ SD) for di- through deca-¹³C₁₂-labeled BDEs internal standards (the mean recovery of mono-¹³C₁₂-labeled BDE internal standard were below 10%), 79% ($\pm 17.1\%$ SD) for tetra- through octa-¹³C₁₂-labeled PCDDs/Fs, and 85.8% ($\pm 14\%$ SD) for tetra- through

octa-¹³C₁₂-labeled PBDDs/Fs, respectively (the mean recovery of tri-¹³C₁₂-labeled BDF internal standard was below 60%).

The linear dynamic range, repeatability, and reproducibility of the final instrumental method was tested with satisfactory results. Five-point calibration curve concentrations, correlation coefficients, relative response factors (RRFi's), and repeatability in relative standard deviations for brominated compounds analyzed by isotope dilution compounds are given in Table 1. Results for the complete set of analytes are given in Tables S-3 and S-4 of the Supporting Information.

Conclusions. The analytical method developed enables sampling and determination of the broad spectrum of brominated and chlorinated dioxins, as well as bromodiphenylethers, including the rarely analyzed coplanar PBDEs, in flue gases from MWCs and other combustion/thermal sources. After employment of additional standards and availability of PBDD/F window-defining solutions, our method should be easily extended to analysis of remaining 2,3,7,8-PBDDs/Fs that have not been reported in the present study, as well as PBDDs/Fs congeners with different substitution patterns. Upon future more wide availability of PBCDDs/Fs standards, the method should be suitable for analysis of mixed bromochlorodibenzo-*p*-dioxins and furans by isotope dilution and HRGC/HRMS, as this rarely investigated class of compounds has physicochemical properties similar to both PCDDs/Fs and PBDDs/Fs. There are very few standard method guidelines for acceptable recoveries of PBDEs and PBDDs/Fs in environmental matrixes; the results of this study are well within the range of recoveries suggested for ¹³C₁₂-labeled PBDE internal standards in the U.S. EPA Method 1614 (25–200%).³⁹ Our results are also not only in the range reported in recent intercalibration studies (40–120%) but also within the values as acceptable thresholds, i.e., between 70% and 120%.^{17,22} The integrated analytical protocol allows isolation of the different groups of analytes from the same sample, their relatively rapid

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automated fractionation, and improvement in the overall cost- and time-effectiveness, without jeopardizing accuracy and robustness.

Our comprehensive congener-specific analysis tool will enable a better understanding of “end-of-life products of brominated flame retardants” in a waste stream and will provide much needed information on levels, fate, and behavior of bromoorganics during incineration of waste containing PBDEs to allow a more comprehensive picture about routes of human exposure to brominated dioxins and brominated dioxin-like compounds.

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SUPPORTING INFORMATION AVAILABLE

Detailed conditions of cleanup and fractionation of target halogenorganics, SIR chromatograms of all analyzed PBDEs, HRGC separation tests between PB_nDF and $PB_{n+2}DE - 2Br$ congeners on 15 and 60 m DB5 columns, compositions of PBDE/PBDD/PBDF presampling, preinjection, and pre-extraction spikes, detailed information on m/z selected for SIR monitoring of PBDE and PBDD/F analytes, compound-specific calibration data of all analyzed bromoorganics, instrumental detection and quantification limits (LOD and LOQ), and average total concentrations of all targets in the combustion flue gas analyzed. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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